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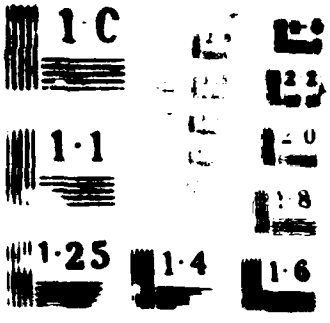
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Thin Walled Benzene Derived Graphite Fibers

M. Shiraishi, M. Endo, M.S. Dresselhaus

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Ultra Thin Carbon fibers, high resolution electron microscopy studies of thin carbon fibers

A brief study has been carried out to investigate the structure of pristine and intercalated thin benzene derived graphite fibers. High resolution transmission electron microscopy techniques were used. The fibers used for this study were prepared by thermal decomposition of benzene onto a substrate seeded with metal particles. The unique feature of the fibers used in this study is that their diameter is only 170 manometers. Fibers used in earlier studies and for most technological applications have generally had diameters more than an order of magnitude larger. Study of the physics of size effects in carbon fibers was a prime motivating force for the current investigation.

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MICROSTRUCTURE OF THIN INTERCALATED BENZENE DERIVED GRAPHITE FIBERS [1]

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Graphite fibers have become increasingly important in recent years for technical applications such as composites. Due to the low fracture toughness of graphite it is profitable to use a dispersion of thin fibers to achieve enhanced mechanical properties of composites. A further motivating force for developing thin fibers is the possibility of producing conducting polymer composites. For such systems both the polymer and the fiber represent conducting pathways. The transport properties of the fiber can be altered radically by intercalation. Hence, the transport properties of a polymer– graphite composite can be controlled. Any intercalated fiber used for bulk technical applications must be air stable and must intercalate uniformly. The purpose of the current study is to investigate the structure of pristine and intercalated thin benzene derived graphite fibers.

The fibers used for this study were prepared by thermal decomposition of benzene onto a substrate seeded with metal particles. The growth processes have been studied elsewhere.[1] The unique feature of the fibers used in this study is that their diameter is only 170 nm. Fibers used in earlier studies and for most technological applications have generally had diameters in the range 2 – 10 μm. The physics of size effects is a prime motivating force for the current investigation.

The structure of the pristine fiber is quite uniform along the fiber length and from fiber to fiber, as shown in Fig. 1a. The average fiber diameter is 170 nm with less than 10% variation. The grain morphology is such that the exposed faces of the fiber are c–faces. This follows directly from surface energy minimization. The average grain length along the fiber axis is ~150 nm. High resolution (002) lattice fringe images on fiber grains show a very high degree of structural order as shown in Fig. 1b. Here the fringes are extremely straight over regions in excess of 40 nm. Crystalline regions of this quality are generally well suited for intercalation.

The transition metal chloride graphite intercalation compounds are known for their air stability. Four transition metal chlorides, $CuCl_2$, $FeCl_3$, $MnCl_2$, $CoCl_2$, have been selected as intercalants for these thin fibers. The primary intent of the intercalation study is to investigate both the stability and structure of the resulting compounds. The intercalants, target stages, intercalation conditions, and results are summarized in Table 1.

The morphology of all the intercalated fibers is quite rough. The structure of $CuCl_2$ intercalated fibers is shown in Fig. 2a. The most pronounced features of the fiber are the expanded and unexpanded regions. The average diameter of the expanded regions is ~250 nm, whereas the diameter of the unexpanded fiber is 100 nm. More careful examination of the expanded regions shows that many are actually cylindrical sheaths wrapped symmetrically around an unexpanded fiber. The lengths of the sheaths vary from 100 to 3000 nm. It is interesting to consider here that the diameter of the unexpanded region is only 60% of the diameter of the pristine fiber. It is unlikely that the Cl_2 gas or $CuCl_2$ in the intercalation ampoule reacts violently with the fibers to reduce their diameters. It is possible, however, that the outer diameter of the fiber intercalated and then regions broke off the fiber as a result of large strains. Selected area electron diffraction on the expanded regions frequently showed intercalant reflections (this will be discussed below) whereas the unexpanded regions never display any intercalant reflections. Hence, it is likely that the full outer region of a given fiber was intercalated.

In all of the fibers either partial or complete deintercalation is observed. Simple calculations show that to achieve the diameter increases observed in the expanded regions, a stage index of 1 or 2 must be achieved prior to deintercalation. However, with only one exception, selected area electron diffraction and high resolution imaging revealed mixed stage structures with a

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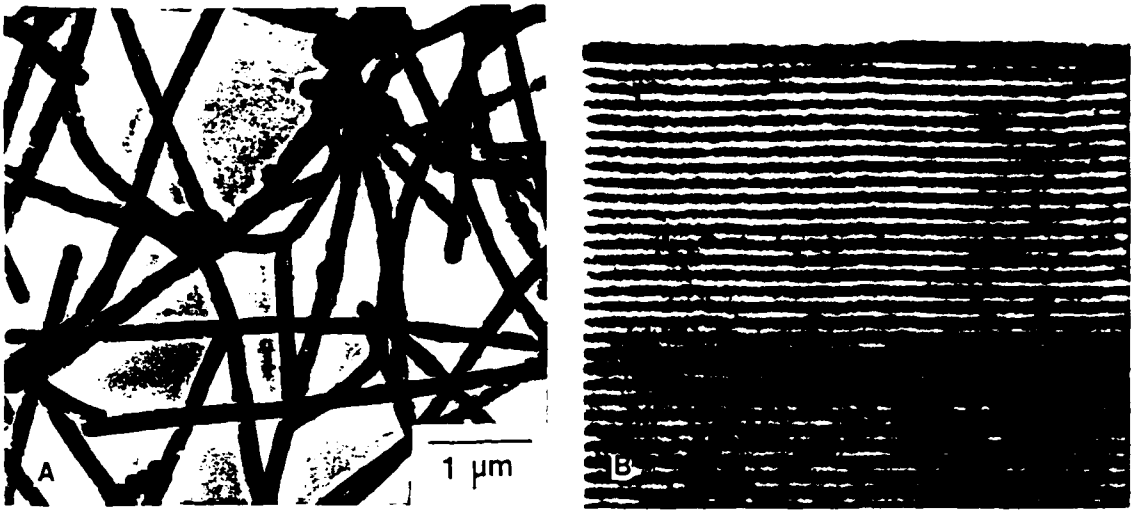


Figure 1: (a) General structure of pristine fibers as observed in bright field TEM. (b) Lattice fringe image of a dislocation–free region of fiber.

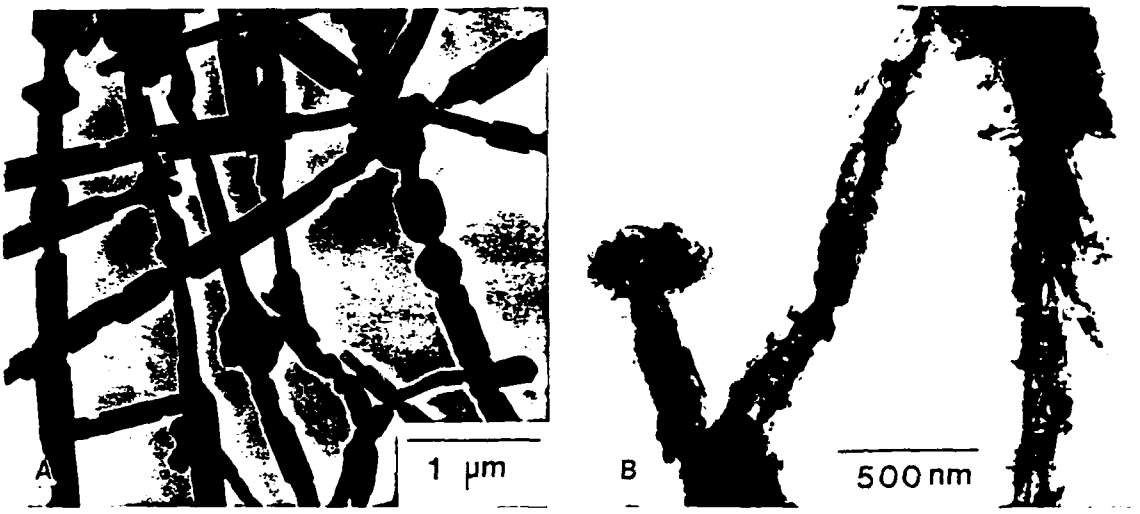


Figure 2: (a) Structure of thin fibers partially intercalated with $CuCl_2$.
(b) Pitted surface structure of thin fibers after exposure to $MnCl_2$.

high stage index ($n \geq 4$). Powder x–ray diffraction patterns also show a mixed stage structure. However, studies of powder x–ray diffraction intensities as a function of time have not been performed.

The results for the $MnCl_2$ and $CoCl_2$ intercalated fibers are quite similar to those discussed above. The one major difference is that the $CoCl_2$ and $MnCl_2$ fibers exhibit a pitted surface structure in regions of otherwise uniform expansion. The pits are ~100 nm long in the direction of the fiber axis as shown in Fig. 2b. The pits may be associated with strain induced fracture at grain boundaries.

The $FeCl_3$ intercalated fibers display expanded and unexpanded regions quite similar to those in the $CuCl_2$ intercalated fibers. Additionally, the $FeCl_3$ intercalated fibers exhibited exfoliated regions with a structure similar to those discussed by Jimenez et al.[2] The exfoliation may occur by the reaction

$$2FeCl_{3,intercalated} = 2FeCl_{2,intercalated} + Cl_{2,gas} \quad (1)$$

The presence of exfoliated fibers represents an additional drawback to the use of these fibers for commercial applications.

Finally, we note that on occasion a pristine fiber with diameter ~300 nm is intermixed with

the 170 nm fibers. These fibers presumably remain in the processing furnace for two or more cycles and experience extra thickening. These large fibers are observed to intercalated uniformly. Additionally, their air stability is very good. This preliminary result suggests that there may be a threshold fiber diameter necessary to produce uniform intercalation and air stability.

The structures of the intercalated fibers are very complicated at the least and probably can only be understood on a phenomenological basis. However, we can conclude that the pristine fibers are excellent candidates for use in composite materials. The nonuniform morphology and rapid desorption of the intercalated thin fibers will most likely prove to be prohibitive for use in many technical applications.

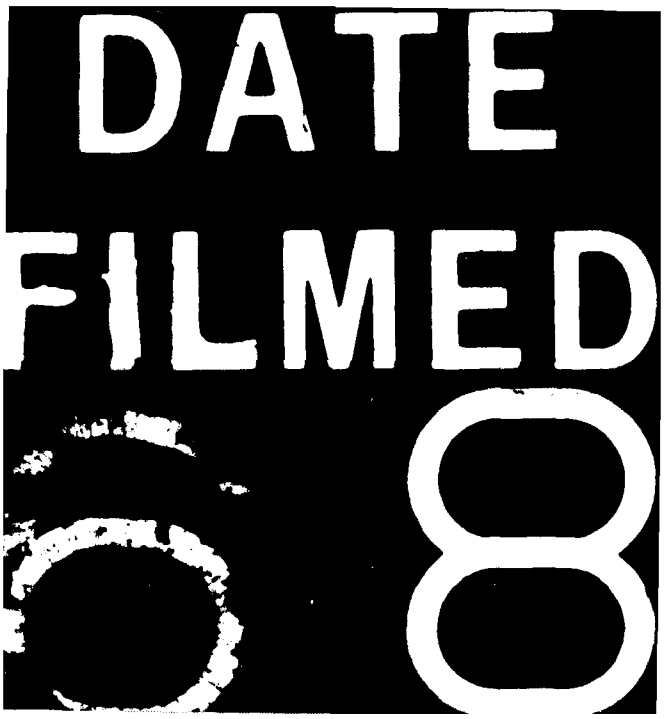
References

[1] M. Endo, and H. Ueno, 1984 MRS Fall Meeting, Extended Abstracts on *Graphite Intercalation Compounds* (ed. P.C. Eklund, M.S. Dresselhaus, and G. Dresselhaus), p. 177.

[2] H. Jiménez-González, J.S. Speck, G. Roth, M.S. Dresselhaus, and M. Endo, accepted for publication in *Carbon*.

Table 1: Table of Results

Intercalant	Target stage	t, T, P_{Cl_2}	Results
$CuCl_2$	2	500°C, 450 torr 3 weeks	•Mixed staging. •Deintercalation. •Nonuniform fiber morphology.
	2	530°C, 100 torr 2 weeks	•Risk control intercalated to pure stage-2. •Deintercalation. •Nonuniform fiber morphology.
$FeCl_3$	2	T_g=350°C, T_f=300° 70 hours, vacuum	•Nonuniform fiber morphology. •Exfoliation. •Deintercalation.
	2	T_g=350°C, T_f=300°C 24 hours, vacuum	•Consistent with above. •Control sample intercalated to stage-2.
$MnCl_2$	2	500°C 525 torr 4 weeks	•Uniform fiber diameter but with a heavily pitted surface. •Thicker fibers have better surface quality. •Deintercalation.
$CoCl_2$	1	500°C 525 torr, 4 weeks	•Rapid deintercalation. •X-ray indicated mixed staging.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